

# Molecular Mechanics and *Ab Initio* Calculations on Cyclopentadienyl Cations

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**ABSTRACT:** We report *ab initio* [MP2(full)/6-31G\*] and force field (MMP2 extended to carbocations) results on the parent and alkylated singlet cyclopentadienyl cations. The *ab initio* results are complemented by force field calculations of 1,3  $\pi$ -interactions and antiaromatic destabilization energies. The antiaromatic destabilization of the singlet cyclopentadienyl cation is larger than that of cyclobutadiene. The MMP2 heats of formation of various cyclopentadienyl cations agree with experimental and *ab initio* data. Two Jahn–Teller distorted isomeric structures with almost identical energies are found for the parent singlet cyclopentadienyl cation. Dynamic and nondynamic correlation calculations employing the CASSCF(4,5)/6-31G\*//MP2(full)/6-31G\* and CASPT2(4,5)/6-31G\*//MP2(full)/6-31G\* levels of theory clearly show the energetic favorability of an allylic structure for the parent singlet cyclopentadienyl cation. Alkylated cyclopentadienyl cations prefer one of the two possible isomeric cyclopentadienyl cation forms. The substitution pattern determines the preferred cyclopentadienyl structure. As a consequence of its strong antiaromatic destabilization the singlet *t*-butylcyclopentadienyl cation is predicted to rearrange to a homoallylic 2-(1-methyl-2,4-cyclopentadienyl)-2-propyl cation. © 1998 John Wiley & Sons, Inc. *J Comput Chem* 19: 1402–1420, 1998

**Keywords:** antiaromatic destabilization energies; singlet–triplet separation; structures and heats of formation; stabilization by 1,3  $\pi$ -overlaps; homoallylic *t*-butylcyclopentadienyl cation structure

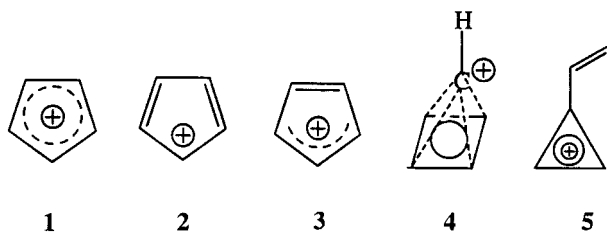
Dedicated to Prof. N. L. Allinger on the occasion of his 70th birthday

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## Introduction

The cyclopentadienyl cation is of basic interest because of its presumably antiaromatic<sup>1,2</sup>  $4\pi$ -electron system. The ground state of this cation was indicated to be a triplet with  $D_{5h}$  symmetry by ESR spectroscopy.<sup>3</sup> High level *ab initio* calculations<sup>4</sup> confirm the lower energy of the  $D_{5h}$  triplet **1** relative to the  $C_{2v}$  singlet structures **2** and **3**. These singlets result from first order Jahn–Teller<sup>5</sup> distortion<sup>6</sup> and have nearly the same energy. Early investigations of the  $C_5H_5^+$  hypersurface<sup>7</sup> using the semiempirical CNDO<sup>8</sup> and MINDO/3<sup>9</sup> methods focused on the three-dimensional aromatic<sup>10</sup> square pyramidal structure **4** with  $C_{4v}$  symmetry, first proposed by Williams<sup>11</sup> and then by Stohrer and Hoffmann.<sup>12</sup> Masamune's  $^{13}C$  NMR investigations<sup>13</sup> of stable ions in superacid media<sup>14</sup> provided experimental evidence for various derivatives of **4**. Maier et al. proposed a distorted square pyramidal structure for a tetra-*t*-butyl derivative of the  $C_5H_5^+$  cation.<sup>13d</sup> However, high level *ab initio* calculations<sup>4</sup> showed that the planar triplet **1** and singlet structures, **2**, and **3** are all lower in energy than **4**. Whereas the vinylcyclopropenyl cation **5** has been suggested to be the most stable  $C_5H_5^+$  isomer,<sup>4c</sup> the most recent high level *ab initio* calculations employing the G2 level of theory<sup>15</sup> found almost identical energies of **1** and **5**<sup>4d</sup>:



We now report both MP2(full)/6-31G\* *ab initio* and force field calculations on the antiaromatic singlet cyclopentadienyl cations as well as their alkylated derivatives. We used a force field method, developed from MM2(82),<sup>16</sup> and parameterized for localized and delocalized classical carbocations.<sup>17</sup> In contrast to earlier carbocation parameterizations,<sup>18,19</sup> which were devised to reproduce strain energies, this method appears to give excellent results, especially for resonance and non-bounded resonance (i.e.,  $\pi$ -overlap between carbons that are not connected by a  $\sigma$ -bond) effects in

delocalized cations.<sup>20</sup> *Ab initio* geometries [MP2(full)/6-31G\*] are reproduced well. The MMP2 SCF calculations allow quantitative estimation of the degree of antiaromaticity in the singlet cyclopentadienyl cations—because of the  $\sigma/\pi$ -separation MMP2 SCF energies refer only to trigonal carbon interactions.

## Methods

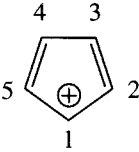
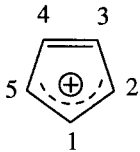
All *ab initio* calculations used the Gaussian-92<sup>21</sup> and Gaussian-94<sup>22</sup> programs on Convex C220, Hewlett-Packard 9000-735, and Cray YMP-864 computers. All optimizations were carried out at the RMP2(full)/6-31G\* level.<sup>23,24</sup> Correlated *ab initio* methods are necessary for the optimization of delocalized cations.<sup>25</sup> All optimized structures were characterized by harmonic frequency computations at HF/6-31G\*//HF/6-31G\*. The energies discussed in the text (see Tables II and V) refer to single point calculations on these geometries (see Tables I and IV) using fourth order Møller–Plesset correction including single, double, triple, and quadruple excitations (MP4sdtq)<sup>26</sup> for molecules up to six carbon atoms, but only MP4sdq<sup>26</sup> for larger molecules.  $\pi$ -Electron densities are based on NLMO/NPA<sup>27</sup> analyses of RHF/6-31G\* wave functions using MP2(full)/6-31G\*-optimized structures. The force field calculations (see Tables I and III–V) were performed with the modified MM2(82) program<sup>28</sup> adapted to a Convex C220.

## Singlet Cyclopentadienyl Cation

The single cyclopentadienyl cation has already been studied by high-level *ab initio* methods.<sup>4</sup> The results suggest that **2** is a minimum, but only slightly more stable than **3**, a transition state.<sup>4</sup> MMP2 finds both **2** and **3** to be minima. Table I lists  $\pi$ -electron densities and geometry parameters of both structures at MMP2 and MP2(full)/6-31G\*.

The geometries obtained by the two theoretical methods agree surprisingly well. The MMP2 heat of formation is 252.6 kcal/mol for **2** and 252.8 kcal/mol for **3**. These values confirm the slight energetic preference of **2** over **3**, found by *ab initio* methods. MMP2 attributes this energy difference to a slightly better  $\pi$ -energy of **2**. In contrast, calculations taking into account both dynamic and nondynamic correlation effects clearly favor **3** over **2**. Whereas the energetic preference of **3** is only

**TABLE I.**  
 $\pi$ -Electron Densities and Geometry Parameters of  $C_5H_5^+$  Singlet Structures (2 and 3) at MP2(full) / 6-31G\* and MMP2.

<div style="display: flex; justify-content: space-around; align-items: center;">   </div>					
$\pi$ -Electron densities					
Atom	MMP2	MP2(full) / 6-31G*	Atom	MMP2	MP2(full) / 6-31G*
C1	0.393	0.350	C1	1.128	1.185
C2	1.089	1.133	C2	0.473	0.439
C3	0.715	0.684	C3	0.964	0.960
Geometry parameters					
Geometric feature	MMP2	MP2(full) / 6-31G*	Geometric feature	MMP2	MP2(full) / 6-31G*
<b>Bonds</b>					
C1 — C2	1.441 Å	1.443 Å	C1 — C2	1.396 Å	1.389 Å
C2 — C3	1.363 Å	1.354 Å	C2 — C3	1.489 Å	1.519 Å
C3 — C4	1.556 Å	1.563 Å	C3 — C4	1.349 Å	1.339 Å
<b>Angles</b>					
C1 — C2 — C3	107.2°	105.9°	C1 — C2 — C3	109.6°	110.7°
C2 — C3 — C4	107.4°	107.9°	C2 — C3 — C4	107.3°	106.6°
C2 — C1 — C5	110.8°	112.3°	C2 — C1 — C5	106.2°	105.4°

2.09 kcal/mol at CASSCF(4,5)/6-31G\*//MP2(full)/6-31G\*, dynamic correlation calculations employing the CASPT2(4,5)/6-31G\*//MP2(full)/6-31G\* level of theory favor **3** by 35.24 kcal/mol over **2**. Single determinant wave functions as employed by the SCF routine of the MMP2 force field and by the MP4sdtq/6-31G\*//MP2(full)/6-31G\* *ab initio* methods are not able to detect the energetic relationship of structures **2** and **3**.

The MMP2 heats of formation of singlets **2** and **3** both agree well with the experimentally determined value (252 kcal/mol<sup>29,30</sup>), despite the fact that triplet **1** should be the ground state. By

evaluating the theoretical enthalpy of the reaction: Glukhovtsev et al. recommended that the experimental  $\Delta H_f^0$  of the  $C_5H_5^+$  triplet should be corrected to 260.9 kcal/mol.<sup>4d</sup> However, this conclusion is debatable, because this value is derived from the experimental heat of formation of the cyclopropenyl cation, which also may be in error. We have therefore compared the *ab initio* energies of the cyclopentadienyl cation isomers with that of the isomeric vinylcyclopropenyl cation **5** (experimental heat of formation: 242 kcal/mol<sup>29,30</sup>) to estimate the heat of formation of **1**.

In excellent agreement with recent high level *ab initio* data,<sup>4d</sup> **1** is 1.2 kcal/mol lower in energy than **5**<sup>31</sup> (Table II). Because the experimental determined heat of formation of the cyclopentadienyl cation is 10 kcal/mol higher than that of **5**, this suggests that the experimental determination cor-



TABLE II.

*Ab Initio* Energies EMP2 (a.u.),<sup>a</sup> EMP4 (a.u.),<sup>b</sup> ECASSCF (a.u.),<sup>c</sup> and ECASPT2 (a.u.),<sup>d</sup> and Number of Imaginary Frequencies (NIMAG), Zero-Point Energies (ZPE, kcal / mol),<sup>e</sup> and Relative *Ab Initio* Energies ( $E_{\text{rel}}$  [kcal / mol]) of Cyclopentadienyl and Related Cations.



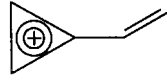

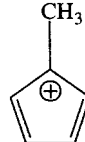
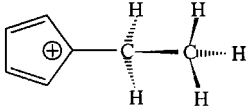
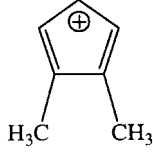

Cation	EMP2 EMP4	NIMAG ZPE	ECASSCF ECASPT2	$E_{\text{rel}}$
 <b>3 C<sub>2v</sub></b>	-192.51986 -192.56633	1 50.1 <sup>f</sup>	-191.93253 -192.57042	7.37
 <b>2 C<sub>2v</sub></b>	-192.52005 -192.56647	0 49.8 <sup>f</sup>	-191.92919 -192.51426	7.28
 <b>5 C<sub>s</sub></b>	-192.53552 -192.57611	0 53.5 <sup>f</sup>	— —	1.23
 <b>1 D<sub>5h</sub> triplet</b>	-192.53843 -192.57807	0 52.7 <sup>f</sup>	— —	0
 <b>6 C<sub>s</sub></b>	-231.72240 -231.77881	0 72.3	— —	—
 <b>7 C<sub>s</sub></b>	-270.89813 -270.92570	0 92.1	— —	11.95
 <b>13 C<sub>2v</sub></b>	-270.90549 -270.93185	0 90.7	— —	8.27
 <b>16 C<sub>2v</sub></b>	-270.91752 -270.94503	0 90.9	— —	0

TABLE II.  
(Continued)


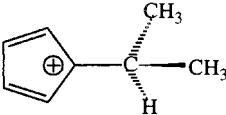
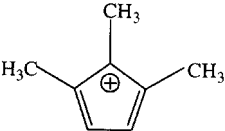
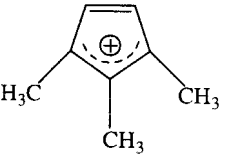
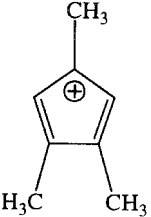

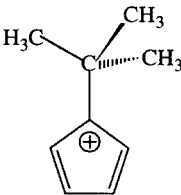
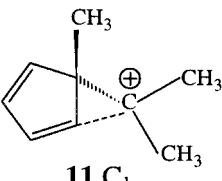
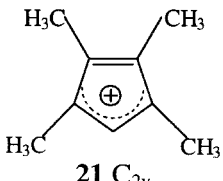
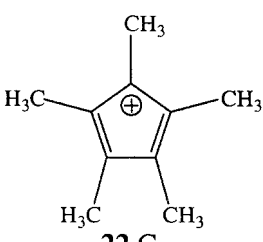
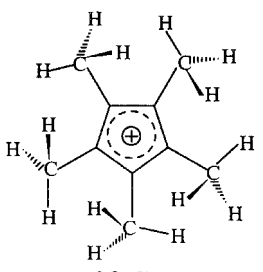
Cation	EMP2 EMP4	NIMAG ZPE	ECASSCF ECASPT2	<i>E</i> <sub>rel</sub>
<div>n-Pro</div> <div></div> <div>8 C<sub>s</sub></div>	<div>−310.07301</div> <div>−310.10594</div>	<div>0</div> <div>111.4</div>	<div>—</div> <div>—</div>	18.29
<div></div> <div>10 C<sub>1</sub></div>	<div>−310.07513</div> <div>−310.10708</div>	<div>0</div> <div>111.0</div>	<div>—</div> <div>—</div>	17.57
<div></div> <div>19 C<sub>s</sub></div>	<div>−310.08542</div> <div>−310.11861</div>	<div>0</div> <div>109.4</div>	<div>—</div> <div>—</div>	10.33
<div></div> <div>18 C<sub>1</sub></div>	<div>−310.09698</div> <div>−310.12900</div>	<div>0</div> <div>109.5</div>	<div>—</div> <div>—</div>	3.82
<div></div> <div>20 C<sub>s</sub></div>	<div>−310.10264</div> <div>−310.13508</div>	<div>0</div> <div>109.3</div>	<div>—</div> <div>—</div>	0
<div>n-Bu</div> <div></div> <div>9 C<sub>s</sub></div>	<div>−349.24611</div> <div>−349.28462</div>	<div>0</div> <div>130.5</div>	<div>—</div> <div>—</div>	22.71

TABLE II.  
(Continued)

Cation	EMP2 EMP4	NIMAG ZPE	ECASSCF ECASPT2	$E_{\text{rel}}$
 <b>12</b> C <sub>5</sub>	-349.24987 -349.28753	1 129.8	— —	20.88
 <b>11</b> C <sub>1</sub>	-349.27431 -349.30201	0 129.7	— —	11.80
 <b>21</b> C <sub>2v</sub>	-349.28331 -349.32081	0 128.1	— —	0
 <b>22</b> C <sub>1</sub>	-388.46256 -388.50466	0 146.6	— —	4.35
 <b>23</b> C <sub>5h</sub>	-388.47258 -388.51159	0 146.7	— —	0

<sup>a</sup>MP2(full) / 6-31G\* // MP2(full) / 6-31G\*.<sup>b</sup>MP4sdtq / 6-31G\* // MP2(full) / 6-31G\* for molecules up to six carbons; for larger molecules MP4sdq / 6-31G\* // MP2(full) / 6-31G\*.<sup>c</sup>CASSCF(4,5) / 6-31G\* // MP2(full) / 6-31G\*.<sup>d</sup>CASPT2(4,5) / 6-31G\* // MP2(full) / 6-31G\*.<sup>e</sup>RHF / 6-31G\* // RHF / 6-31G\*.<sup>f</sup>MP2(fc) / 6-31G\* // MP2(full) / 6-31G\*.

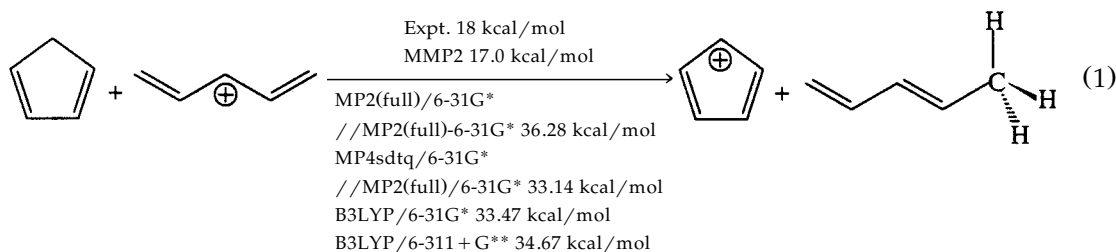
responds to a  $C_{2v}$  singlet structure, **2** or **3**, both of which are higher in energy than **5**.

The net 1,3  $\pi$ -overlap effects stabilize the singlet cyclopentadienyl cations by  $-11.1$  kcal/mol for **2** and  $-11.2$  kcal/mol for **3**. These values are reduced slightly relative to that of the open-chain 1,3-pentadien-5-yl cation ( $-12.6$  kcal/mol) because of the destabilizing 1,3  $\pi$ -interactions between C2 and C5 in **2** and between C1—C3 and C1—C4 in **3** (see Table I for numbering). The C1—C3 and C1—C4 1,3  $\pi$ -interactions stabilize **2** by  $-18.6$  kcal/mol. The C1—C3, C1—C4, and C2—C5 1,3  $\pi$ -interactions in **3** result in an  $-18.5$  kcal/mol energy lowering. These strong stabilizing effects are reduced by all other 1,3  $\pi$ -interactions, which are energetically unfavorable.

We examined the antiaromaticity of the cyclopentadienyl cation by comparing its  $\pi$ -energy with that of the acyclic 1,3-pentadien-5-yl cation

(because MMP2 does not include  $\sigma$ -electrons in the quantum mechanics treatment, these two structures can be regarded as isoelectronic  $\pi$ -systems). Table III lists the MMP2  $\pi$ -energies of these cations and some neutral molecules.

The MMP2  $\pi$ -energy increase on hypothetical ring closure of the 1,3-pentadien-5-yl cation,  $+18.7$  kcal/mol (difference in  $\pi$ -energies, Table III), is a measure of the antiaromatic destabilization energy in the cyclopentadienyl system. Evaluated analogously, the antiaromatic  $\pi$ -destabilization energy of cyclobutadiene is only  $+9.1$  kcal/mol (see Table III). This suggests that the antiaromaticity in the cationic singlet cyclopentadienyl system is greater than in neutral cyclobutadiene. The isodesmic equations [eqs. (1) and (2)] demonstrate this stronger antiaromatic destabilization effect in the cyclopentadienyl system<sup>32,33</sup>:



$\Delta H_f$  (MMP2)

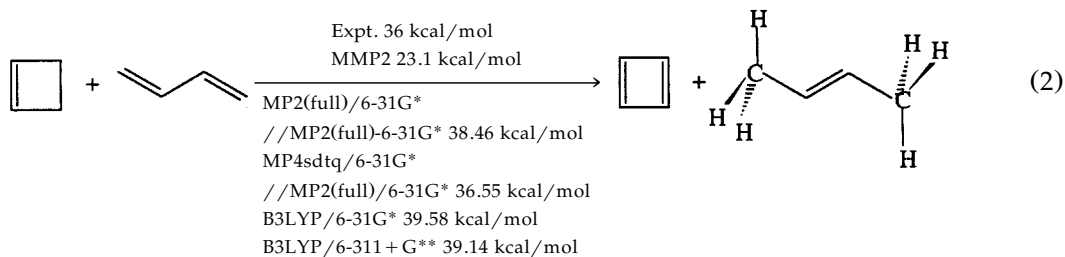
in kcal/mol:	32.7	220.1	252.6	17.2
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$\Delta H_f^0$  (expt.)

in kcal/mol:	32 $\pm$ 0.1 <sup>33</sup>	220 $\pm$ 2 <sup>29,30,34</sup>	252 $\pm$ 2 <sup>29,30,34</sup>	18 $\pm$ 0.1 <sup>33</sup>
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The difference in eq. (1) between the *ab initio* data, on the one hand, and the experimental and MMP2 results, on the other hand, is due to the uncertainty of the experimental heat of formation of the singlet cyclopentadienyl cation, which might

be significantly higher than 252 kcal/mol, and the adaptation of the MMP2 heats of formation to the experimental values. Analogous derivations are found in eq. (3):



$\Delta H_f$  (MMP2)

in kcal/mol:	38.4	25.1	89.0	-2.4
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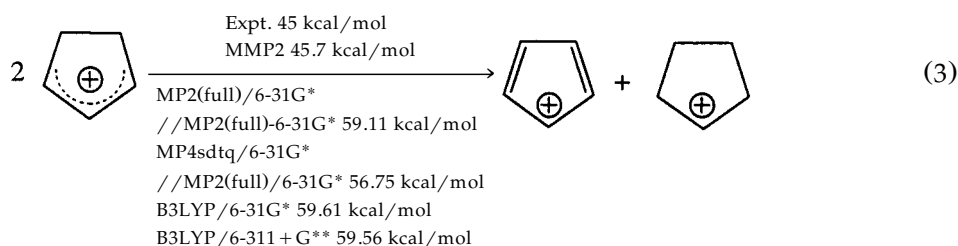
$\Delta H_f^0$  (expt.)

in kcal/mol:	37 $\pm$ 0.1 <sup>33</sup>	26 $\pm$ 0.1 <sup>33</sup>	102 $\pm$ 1 <sup>32</sup>	-3 $\pm$ 0.1 <sup>33</sup>
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Magnetic susceptibility exaltations<sup>35</sup> are uniquely associated with aromatic and antiaromatic behavior of molecules.<sup>36</sup> The exaltation,  $\Lambda$ , is defined as the difference between the bulk magnetic susceptibility (e.g., obtained by IGLO<sup>37</sup> calculations) of a compound and the susceptibility estimated from an increment system for the structural components.<sup>38</sup> The paramagnetic susceptibility exaltation,  $\Lambda$ , computed for the singlet cyclopentadienyl cation<sup>39</sup> (+32.6 ppm cgs) is higher than that of cyclobutadiene<sup>40</sup> (+18.0 ppm cgs). Although  $\Lambda$  depends on the square of the ring area, the antiaromatic destabilization in the singlet cy-

clopentadienyl cation evidently is larger than that in cyclobutadiene.

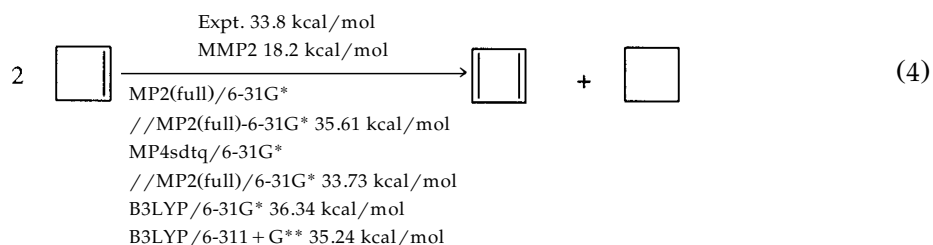
The antiaromatic destabilization energies obtained by homodesmotic equations<sup>39</sup> [eqs. (3) and (4)] give the same trend as the MMP2 values (cyclobutadiene: +36.3 kcal/mol; singlet cyclopentadienyl cation: +56.7 kcal/mol). Note that the data obtained by the different methods cannot be compared directly, because the MMP2 values only refer to  $\pi$ -effects. Nevertheless, MMP2 gives 45.7 kcal/mol for the total antiaromatic destabilization energy of the cyclopentadienyl cation [eq. (3)], and of 18.2 kcal/mol for cyclobutadiene [eq. (4)]:



$\Delta H_f$ (MMP2)			
in kcal/mol:	198.5	252.6	190.1
$\Delta H_f^0$ (expt.)			
in kcal/mol:	$199 \pm 2^{29,30,34}$	$252 \pm 2^{29,30,34}$	$191 \pm 2^{29,30,34}$

The deviation of the MMP2 heat of formation of cyclobutadiene (89.0 kcal/mol) from the value given by Glukhovtsev et al.<sup>32</sup> (102 kcal/mol) re-

flects the differences in eq. (4) between MMP2 and the various *ab initio* methods. Analogous differences are found in eq. (2):

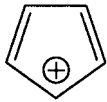

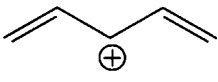
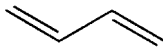



$\Delta H_f$ (MMP2)			
in kcal/mol:	38.4	89.0	6.0
$\Delta H_f^0$ (expt.)			
in kcal/mol:	$37 \pm 0.1^{33}$	$102 \pm 1^{32}$	$6 \pm 0.1^{33}$

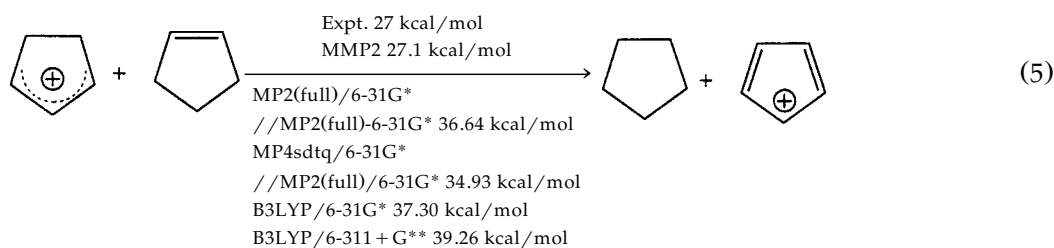


TABLE III.

MMP2  $\pi$ -Energies [ $E_\pi$  in kcal/mol], MMP2 Heats of Formation [ $\Delta H_f$  (MMP2) in kcal/mol], and Experimental Heats of Formation [ $\Delta H_f$  (expt.) in kcal/mol], of Some Cationic and Neutral  $\pi$ -Systems.

Molecule	$E_\pi$	$\Delta H_f$ (MMP2)	$\Delta H_f$ (expt.)
	-171.9	252.6	252
	-171.6	252.8	—
	-190.6	220.1	220
	-117.9	25.1	26
	-108.8	89.0	102

The isodesmic equation [eq. (5)] also demonstrates the large antiaromatic destabilization effect in the cyclopentadienyl system<sup>39</sup>:



$\Delta H_f$ (MMP2)				
in kcal/mol:	198.5	8.8	-18.3	252.6
$\Delta H_f^0$ (expt.)				
in kcal/mol:	$199 \pm 2^{34}$	$8 \pm 0.1^{33}$	$-18 \pm 0.1^{33}$	$252 \pm 2^{34}$

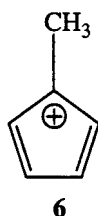
## Substitution by One Alkyl Group

### METHYLCYCLOPENTADIENYL CATION

The MMP2 and *ab initio* results agree that the  $C_s$  singlet methylcyclopentadienyl cation **6** has a localized cyclopentadienyl structure; an allylic

minimum could not be found by either method. The  $\pi$ -charge of C1 is increased relative to **2** (cf. the  $\pi$ -electron densities in Table I) due to a polarization of the  $\pi$ -electrons as a result of hyperconjugation. This is the reason for the lack of an isomeric allylic-type singlet structure at MP2(full)/6-31G\* and at MMP2. Furthermore, the  $\pi$ -charges

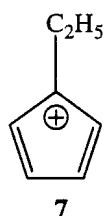
of C3 and C5 (cf. Table IV) are small; as a result, the C3—C5 bond shortens slightly relative to **2** (cf. C—C bond lengths in Tables I and IV). Structure **6** has one methyl C—H bond perpendicular to the planar cyclopentadienyl system. Table IV gives C—C bond lengths and  $\pi$ -electron densities at MP2(full)/6-31G\* and MMP2 for **6** as well as for many other cations (discussed later).



MMP2 results on open-chain allyl cations have shown that hyperconjugating alkyl groups reduce stabilization by 1,3  $\pi$ -overlap.<sup>41</sup> This tendency can also be observed in the cyclopentadienyl system. The MMP2 calculations give a nonbonded resonance stabilization of  $-8.5$  kcal/mol for **6**, significantly lower than that of **2** ( $-11.1$  kcal/mol). Further results on the allyl system have shown that the heats of formation of cations can be estimated from *ab initio* methods.<sup>41</sup> We applied this method to alkylated cyclopentadienyl cations and compared the heats of formation obtained with those at MMP2 (cf. Table V). The MMP2 heat of formation of the methylcyclopentadienyl cation (238.9 kcal/mol) agrees well with the *ab initio* value (237.3 kcal/mol).

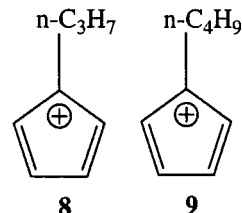
### ETHYLCYCLOPENTADIENYL CATION

The *ab initio* calculations gave C<sub>s</sub> minimum **7** for the ethylcyclopentadienyl cation (cf. Table IV). Nonbonded resonance stabilization in **7** was calculated to be insignificantly lower by MMP2 ( $-8.1$  kcal/mol) than in **6** ( $-8.5$  kcal/mol) because of moderately stronger hyperconjugation. The MMP2 heat of formation (228.7 kcal/mol) was found to be close to the MP4sdq/6-31G\*//MP2(full)/6-31G\* value (228.3 kcal/mol; cf. Table V).



### *n*PROPYL- AND *n*-BUTYLCYCLOPENTADIENYL CATIONS

Minima analogous to **7** were found for the *n*-propyl- and *n*-butylcyclopentadienyl cations (structures **8** and **9**; cf. Table IV). The geometries are closely analogous to **7** with the exception of moderately stronger C—C hyperconjugative lengthening at MP2(full)/6-31G\*. MMP2 gives almost identical  $\pi$ -energies ( $-187.7$  kcal/mol) and nonbonded resonance stabilization ( $-8.1$  kcal/mol) for **7**, **8**, and **9**.



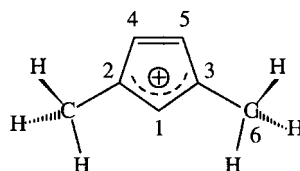
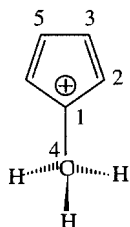
The MMP2 heats of formation of **8** (220.6 kcal/mol) and **9** (214.7 kcal/mol) are close to the values obtained by *ab initio* methods (**8**: 220.4 kcal/mol; **9**: 214.6 kcal/mol). Table V lists the MMP2 and the *ab initio* heats of formation (MP4/6-31G\*//MP2(full)/6-31G\*) of the alkylated cyclopentadienyl cations as well as data for the reference molecules.

The heats of formation calculated by MMP2 and the *ab initio* method (MP4/6-31G\*//MP2(full)/6-31G\*) agree well. A maximum deviation of 3.0 kcal/mol is found for the 1,2,3-trimethylcyclopentadienyl cation (Table V).

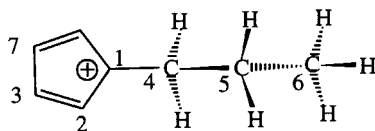
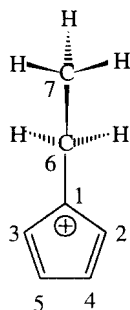
### 2-PROPYLCYCLOPENTADIENYL CATION

The C<sub>1</sub> 2-propylcyclopentadienyl cation conformation **10** has one hyperconjugating C—C bond perpendicular to the planar cyclopentadienyl system [MP2(full)/6-31G\*]. In contrast, MMP2 favors the C<sub>s</sub> alternative with two symmetrical hyperconjugating C—C bonds. Figure 1 lists interesting geometric parameters of this and other cations obtained by the two methods.

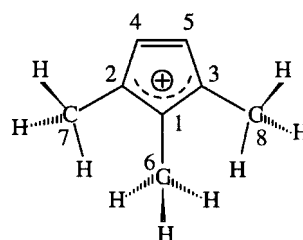
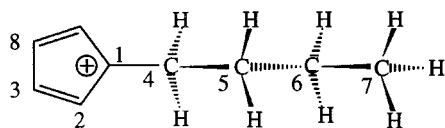
The *ab initio* geometry has one small and one large C-sp<sup>3</sup>—C-sp<sup>3</sup>—C-sp<sup>3</sup> angle resulting from strong C—C hyperconjugation, whereas MMP2 computes two identical angles that deviate only minimally from the tetrahedral value. The MMP2 heat of formation of **10** (219.8 kcal/mol) is close to the MP4sdq/6-31G\*//MP2(full)/6-31G\* value (219.7 kcal/mol; cf. Table V). Both methods agree that **10** is about 0.8 kcal/mol more stable than **8**.

**TABLE IV.****C — C Bond Lengths and  $\pi$ -Electron Densities of Alkylated Cyclopentadienyl Cations at MP2(full) / 6-31G\* (MP2) and MMP2.**

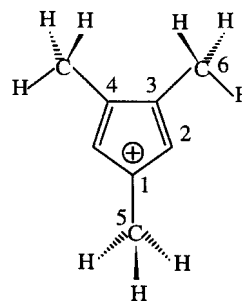
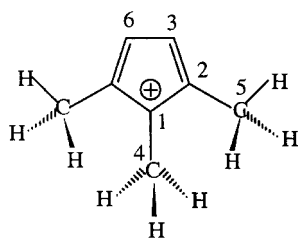
Bond lengths / Å					
Bond	MP2	MMP2	Bond	MP2	MMP2
C1 — C2	1.458	1.454	C1 — C3	1.390	1.401
C2 — C3	1.350	1.359	C3 — C5	1.520	1.492
C3 — C5	1.541	1.544	C4 — C5	1.338	1.347
C1 — C4	1.450	1.458	C3 — C6	1.468	1.465
$\pi$ -Electron densities					
Carbon	MP2	MMP2	Carbon	MP2	MMP2
C1	0.298	0.296	C1	1.204	1.254
C2	1.129	1.128	C2	0.502	0.407
C3	0.721	0.721	C4	0.963	0.966



Bond lengths / Å					
Bond	MP2	MMP2	Bond	MP2	MMP2
C1 — C2	1.461	1.455	C1 — C2	1.463	1.455
C2 — C4	1.349	1.359	C2 — C3	1.349	1.359
C4 — C5	1.533	1.543	C3 — C7	1.528	1.543
C1 — C6	1.436	1.458	C1 — C4	1.426	1.458
C6 — C7	1.591	1.560	C4 — C5	1.613	1.564
			C5 — C6	1.529	1.531
$\pi$ -Electron densities					
Carbon	MP2	MMP2	Carbon	MP2	MMP2
C1	0.252	0.292	C1	0.266	0.291
C2	1.124	1.130	C2	1.120	1.130
C4	0.737	0.725	C3	0.745	0.724

TABLE IV.  
(Continued)

Bond lengths / Å					
Bond	MP2	MMP2	Bond	MP2	MMP2
C1 — C2	1.464	1.455	C1 — C2	1.398	1.397
C2 — C3	1.349	1.359	C1 — C3	1.398	1.397
C3 — C8	1.523	1.543	C2 — C4	1.520	1.488
C1 — C4	1.420	1.458	C3 — C5	1.520	1.488
C4 — C5	1.621	1.564	C4 — C5	1.335	1.347
C5 — C6	1.537	1.533	C1 — C6	1.498	1.491
C6 — C7	1.526	1.533	C2 — C7	1.461	1.461
			C3 — C8	1.461	1.461
$\pi$ -Electron densities					
Carbon	MP2	MMP2	Carbon	MP2	MMP2
C1	0.222	0.291	C1	1.157	1.242
C2	1.116	1.130	C2	0.445	0.411
C3	0.762	0.724	C3	0.443	0.410
			C4	0.966	0.968
			C5	0.963	0.968



Bond lengths / Å					
Bond	MP2	MMP2	Bond	MP2	MMP2
C1 — C2	1.466	1.451	C1 — C2	1.443	1.452
C2 — C3	1.354	1.358	C2 — C3	1.356	1.364
C1 — C4	1.451	1.457	C3 — C4	1.568	1.570
C2 — C5	1.492	1.488	C1 — C5	1.460	1.462
C3 — C6	1.535	1.538	C3 — C6	1.473	1.472
$\pi$ -Electron densities					
Carbon	MP2	MMP2	Carbon	MP2	MMP2
C1	0.288	0.320	C1	0.352	0.313
C2	1.096	1.095	C2	1.150	1.190
C3	0.746	0.750	C3	0.664	0.653

**TABLE V.**

Heats of Formation [ $\Delta H_f$  (MMP2)<sup>a,b</sup> and  $\Delta H_f$  (MP4)<sup>a,c</sup> in kcal / mol] of Alkylated Cyclopentadienyl Cations, Reference Cations for *Ab Initio* Calculations, Their *Ab Initio* Energies (EMP4)<sup>d</sup>, and Their Experimental Heats of Formation,<sup>e</sup> [ $\Delta H_f$  (expt.)].

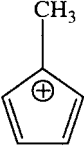

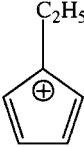
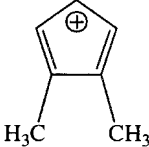

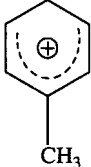
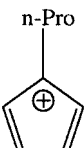
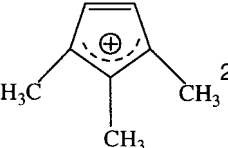
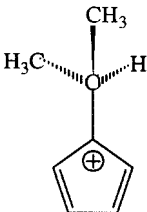
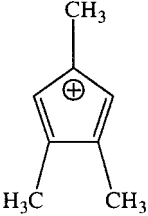
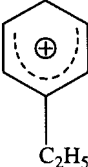
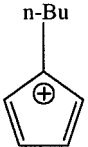
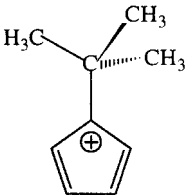
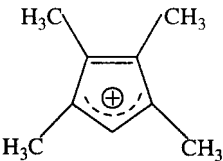
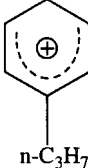
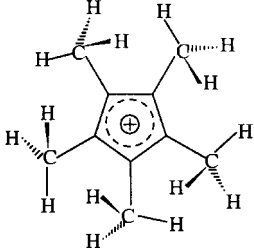
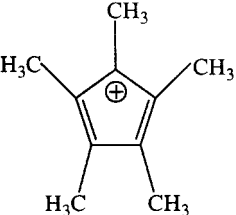
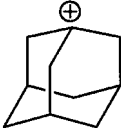
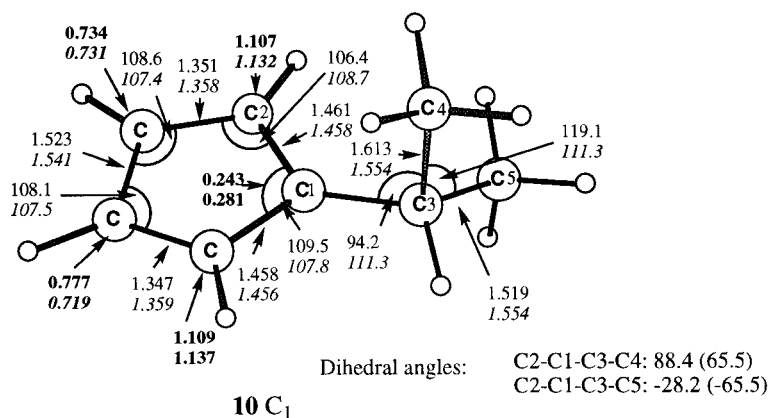
Cation	$\Delta H_f$ (MMP2)	$\Delta H_f$ (MP4)	Reference cation	EMP4 / a.u.	$\Delta H_f$ (expt.)
	238.9	237.2 <sup>f</sup>		-231.83185 <sup>f</sup>	204
	228.7	228.3			
	224.3	224.5			
	218.1	216.2		-270.98997	188
	220.6	220.4			
	209.0	206.0			
	219.8	219.7			

TABLE V.  
(Continued)

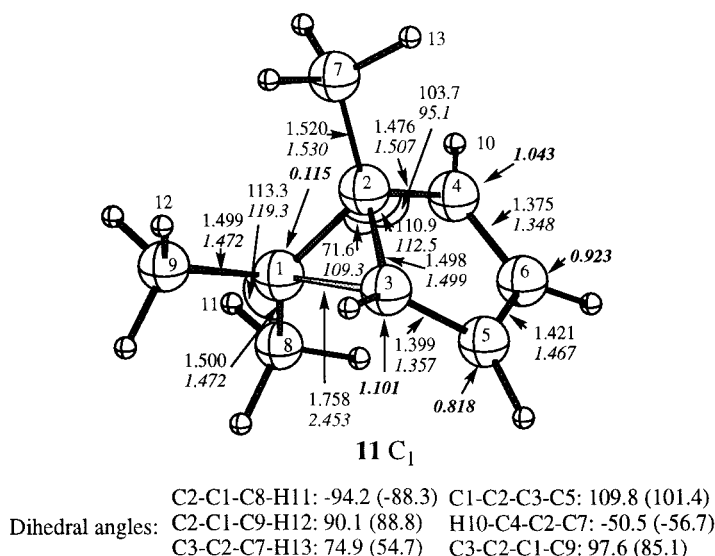
Cation	$\Delta H_f$ (MMP2)	$\Delta H_f$ (MP4)	Reference cation	EMP4 / a.u.	$\Delta H_f$ (expt.)
	197.8	202.1		-310.16877	181
	214.7	214.6			
	212.2	212.7 <sup>f</sup>			
	194.5	191.8		-349.34764	175
	—	184.9			
	187.9	189.1		-388.55250	159

<sup>a</sup>Values in kcal/mol. <sup>b</sup>MMP2 heat of formation. <sup>c</sup>Heat of formation obtained by MP4sdq/6-31G\*\*/MP2(full)/6-31G\* calculations.<sup>d</sup>Values at MP4sdq/6-31G\*\*/MP2(full)/6-31G\*. <sup>e</sup>See refs. 29 and 30. <sup>f</sup>Values at MP4sdq/6-31G\*\*/MP2(full)16-31G\*. <sup>g</sup>The *ab initio* heat of formation was calculated for a C<sub>s</sub> structure, which proved to be a transition state at MP2(full)/6-31G\*, because no minimum for this cation could be found at MP2(full)/6-31G\*.

## 2-Propylcyclopentadienyl Cation



## 2-(1-Methyl-2,4-cyclopentadienyl)-2-propyl Cation

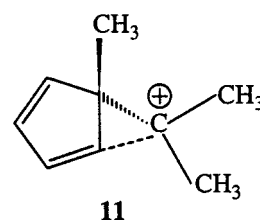


**FIGURE 1.** Geometries<sup>a</sup> and  $\pi$ -electron densities<sup>b</sup> of alkylated cyclopentadienyl cations at MMP2<sup>c</sup> and MP2(full) / 6-31G\*. <sup>a</sup>Bond lengths in angstroms; angles and dihedral angles in degrees. <sup>b</sup>Bold values:  $\pi$ -electron densities. <sup>c</sup>Italics values: MMP2 values; the MMP2 dihedral angles are given in parentheses.

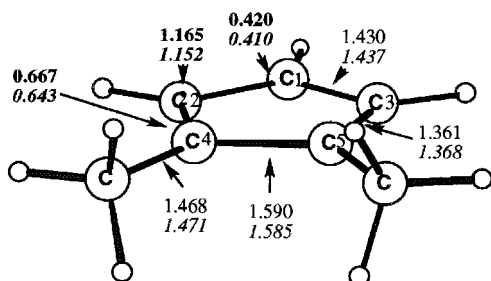
***t*-BUTYLCYCLOPENTADIENYL CATION**

We were not able to locate a *t*-butylcyclopentadienyl *minimum* at MP2(full)/6-31G\*. Methyl group migration during optimization gave the 2-(1-methyl-2,4-cyclopentadienyl)-2-propyl cation (structure **11**; cf. Fig. 1) instead of the *t*-butylcyclopentadienyl cation **12**. The C1—C2—C3 angle in **11** [MP2(full)/6-31G\*: 71.6°] deviates strongly from the tetrahedral value as a consequence of the strong homoallylic 1,3  $\pi$ -overlap of C1 with the C3—C5 double bond. The nonclassical character of the 2-(1-methyl-2,4-cyclopentadienyl)-2-propyl cation **11** is evident. The C1—C3 distance [MP2(full)/6-31G\*: 1.758 Å] is shortened dra-

cally due to the strong 1,3  $\pi$ -overlap of these two carbons. MMP2 computes stabilizing nonbonded resonance interactions of -13.4 kcal/mol, but is not able to reproduce the short C1—C3 distance (MMP2: 2.453 Å).

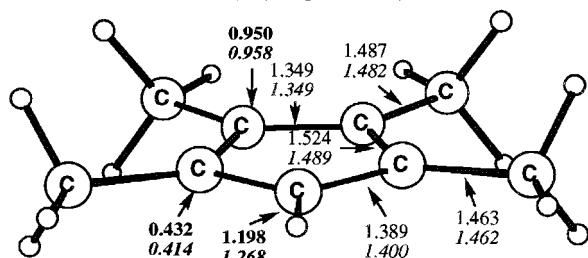


### 1,2-Dimethylcyclopentadienyl Cation



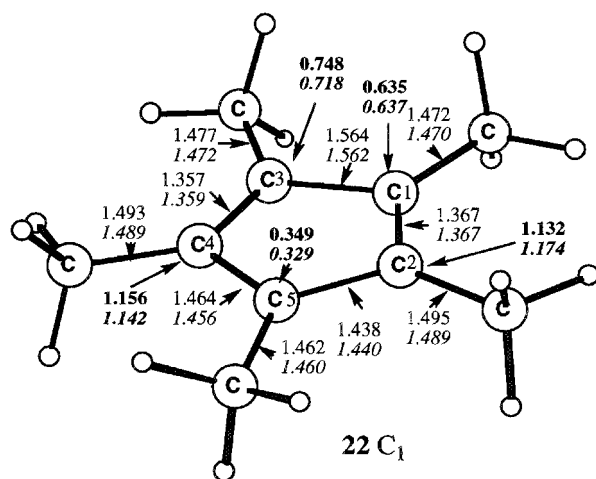
### 13 C<sub>2v</sub>

### Tetramethylcyclopentadienyl Cation



## 21 C<sub>2v</sub>

### Pentamethylcyclopentadienyl Cation

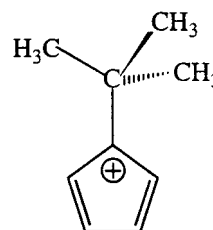


22 C<sub>1</sub>

**FIGURE 1.** Continued.

MMP2 is not applicable to the rearrangement of the *t*-butylcyclopentadienyl cation **12** to **11**. Clearly defined fixed bonds, needed as MMP2 input, cannot be broken. However, the MMP2 heat formation of **12** is 12.1 kcal/mol higher than that of **11** (200.1 kcal/mol), and the rearrangement is favored thermodynamically. MMP2 finds a C<sub>s</sub> symmetry for **12** with one methyl carbon positioned in the cyclopentadienyl plane and with two symmetrical hyperconjugating C—C bonds. This C<sub>s</sub> structure is a transition state at MP2(full)/6-31G\*, 9.1 kcal/mol higher than **11** [MP4sdq/6-31G\*//MP2(full)/

6-31G\*]. The strong antiaromatic destabilization in the cyclopentadienyl system contributes to the rearrangement to a homoallylic 2-propyl cation structure.



12

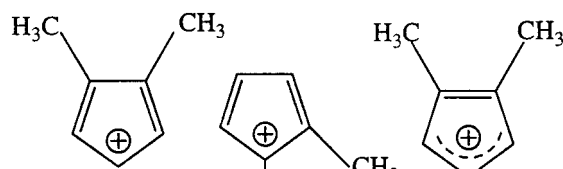
### Substitution by Two Methyl Groups

# SINGLET 1,2-DIMETHYLCYCLOPENTADIENYL CATION

The  $C_{2v}$  singlet 1,2-dimethylcyclopentadienyl cation **13** has one methyl C—H bond of each methyl group eclipsed toward the C—C bonds of a localized cyclopentadienyl cation structure (cf. Fig. 1). The C4—C5 bond is significantly elongated, which we regard to be a consequence of the increasing positive charges of these two carbons (cf. results for the 1,2,4-trimethylcyclopentadienyl and pentamethylcyclopentadienyl cations).

The MMP2 heat of formation (224.3 kcal/mol) for **13** agrees well with the *ab initio* estimate (224.5 kcal/mol; cf. Table V). The MMP2 nonbonded resonance stabilization,  $-9.3$  kcal/mol, is slightly larger than the corresponding effects in the monoalkylcyclopentadienyl cations.

In contrast to the *ab initio* optimizations, MMP2 gives different isomeric 1,2-dimethylcyclopentadienyl cations. However, the *ab initio* minimum is recognized to be the global minimum by MMP2: **13** is 0.5 kcal/mol lower in energy than **14**, and 10.6 kcal/mol more stable than **15**.



13

14

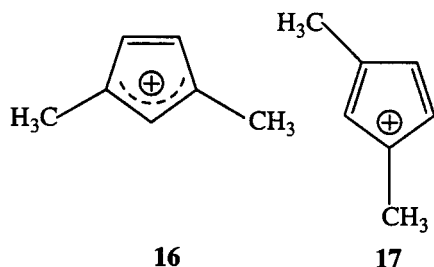
15



### 1,3-DIMETHYLCYCLOPENTADIENYL CATION

In contrast to the monoalkylated cyclopentadienyl cations, the 1,3-dimethylcyclopentadienyl cation favors an allylic structure with  $C_{2v}$  symmetry (**16**, Table IV). This cation is 8.3 kcal/mol lower in energy than **13** at MP4sdq/6-31G\*//MP2(full)/6-31G\* (MMP2: 6.2 kcal/mol) as a consequence of the stronger stabilizing hyperconjugative interactions. The MMP2 1,3  $\pi$ -overlap stabilization of the 1,3-dimethylcyclopentadienyl cation,  $-7.1$  kcal/mol, is moderately lower than that of the 1,2-dimethylcyclopentadienyl cation, also as a consequence of the stronger hyperconjugative interactions.

In contrast to the *ab initio* results, MMP2 finds a second 1,3-dimethylcyclopentadienyl cation minimum with a localized structure (isomer **17**). However, **16** is 1.9 kcal/mol lower in energy than **17**.



### Polymethyl Substitution

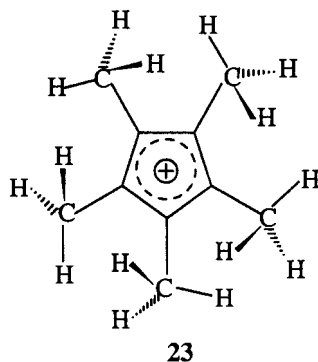
Two 1,2,3-trimethylallyl cation minima were found (cf. Table IV). The more stable isomer **18** has an allylic structure and is 6.5 kcal/mol [MP4sdq/6-31G\*//MP2(full)/6-31G\*] lower in energy than the cyclopentadienyl isomer **19** (MMP2: 2.3 kcal/mol). The MMP2 heat of formation (209.0 kcal/mol) of **18** is 3.0 kcal/mol higher than the *ab initio* value (cf. Table V). The 1,3  $\pi$ -overlap stabilization for the allylic structure is  $-7.6$  kcal/mol.

The  $C_s$  1,2,4-trimethylcyclopentadienyl cation **20** (cf. Table IV) is closely related to **13**. The C3—C4 bond is elongated (MP2(full)/6-31G\*: 1.568 Å; MMP2: 1.570 Å) as a result of charge–charge repulsions. However, this effect is smaller than in **13**, because the methyl group attached to C1 reduces the  $\pi$ -charges of C3 and C4. The MMP2 non-bonded  $\pi$ -resonance stabilization ( $-7.1$  kcal/mol) is slightly smaller than that in **18**. The MMP2 heat of formation (197.8 kcal/mol) may be somewhat

too low [MP4sdq/6-31G\*//MP2(full)/6-31G\*: 202.1 kcal/mol; cf. Table V].

While an allylic  $C_{2v}$  structure **21** could be optimized for the singlet tetramethylcyclopentadienyl cation, the singlet pentamethylcyclopentadienyl cation has a localized  $C_1$  structure **22** (cf. Fig. 1). This cation is related to **20** electronically and sterically. The bond C1—C3 is significantly elongated [MP2(full)/6-31G\*: 1.564 Å; MMP2: 1.562 Å]. The bond elongations in **13**, **20**, and **22** are directly related to the positive  $\pi$ -charges of the participating carbons. Therefore, we conclude that charge–charge repulsions are the driving force for these bond elongations. The MMP2 stabilization energies by 1,3  $\pi$ -interactions are  $-6.9$  kcal/mol for **21** and  $-7.2$  kcal/mol for **22**. The MMP2 heats of formation for both cations agree with *ab initio* values (cf. Table V).

Like the parent cyclopentadienyl cation, a  $C_{5h}$  pentamethylcyclopentadienyl cation triplet **23** is more stable than the  $C_1$  singlet **22**. The hyperconjugating methyl groups do not reduce the singlet–triplet separation of **22** and **23** significantly compared with the parent cyclopentadienyl system. The energy difference between **23** and **22** at MP4sdq/6-31G\*//MP2(full)/6-31G\* +  $\Delta$ ZPE (RHF/6-31G\*) is 4.2 kcal/mol, whereas the corresponding triplet–singlet energy difference of **1** and **2** is 4.4 kcal/mol.



### Conclusions

In agreement with previous studies,<sup>4</sup> two Jahn–Teller electronic structures with almost identical energies are found for the parent singlet cyclopentadienyl cation at MP2(full)/6-31G\* and at MMP2. Calculations taking into account both dynamic and nondynamic correlation effects favor an

allylic ground state for the singlet cyclopentadienyl cation clearly over a localized cyclopentadienyl cation structure. Alkylated cyclopentadienyl cations are characterized by one of the two possible cyclopentadienyl cation structures. The substitution pattern of the alkyl substituents determines the preferred structure of the cyclopentadienyl system. Significant energy differences were found for two 1,2,3-trimethylcyclopentadienyl cation structures. Only one minimum was found for the other alkylated cyclopentadienyl systems.

The force field and *ab initio* geometries of singlet cyclopentadienyl cations are similar. Therefore, MMP2 should provide good starting geometries for *ab initio* refinement. The force field treatment complements the *ab initio* calculations by evaluating nonbonded resonance and antiaromatic destabilization effects. Like the allyl system,<sup>41</sup> the MMP2 1,3  $\pi$ -overlap energies are reduced by hyperconjugating alkyl groups. The antiaromatic destabilization in the cyclopentadienyl system is stronger than in the neutral cyclobutadiene. The lack of a *t*-butylcyclopentadienyl cation minimum structure at MP2(full)/6-31G\* is an important consequence of the strong antiaromatic destabilization in the cyclopentadienyl system. Instead, a homoallylic 2-(1-methyl-2,4-cyclopentadienyl)-2-propyl cation is obtained by rearrangement from methyl group migration.

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$$\square + 4\text{CH}_4 \rightarrow 2\text{H}_3\text{C}-\text{CH}_3 + 2\text{H}_2\text{C}=\text{CH}_2$$
 at QCISD(T)/6-311+G(3df,2p)//MP2(full)6-31G\*, was  $102 \pm 1$  kcal/mol according to M. N. Glukhovtsev, S. Laiter, A. Pross, *J. Phys. Chem.*, **99**, 6828 (1995).
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